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First-principles calculation of the geometric and electronic structure of the Be(0001) surface

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Linearized-augmented-plane-wave calculations for a nine-layer Be(0001) slab agree with the unusual experimental finding of a substantial outer-layer expansion relative to the truncated bulk lattice. They imply that the separation between the outer two layers should be 3.9% larger than in the bulk, while the second- to third-layer separation should be 2.2% larger. The surface expansion is accompanied by demotion of p_σ to s electrons on outer-layer Be's. The surface Be's loss of three neighbors makes the energy cost of s- to p_σ-electron promotion, which is necessary for the formation of strong bonds to the next layer down, less profitable than in the bulk.

I. INTRODUCTION

There are at least three simple ways of explaining why the outer-layer separation at a crystal surface should contract relative to the truncated-bulk-lattice, or "ideal," layer separation. The first is that it is an electrostatic result of the Smoluchowski effect.[1,2] That is, when one cuts a crystal to form a surface, the electronic charge density relaxes so as to weaken its corrugation. This is because electrons can reduce their kinetic energy by reducing the curvature of their wave functions. The smoothing of the electron charge density is equivalent to taking charge from the regions directly above surface atoms and moving it to the hollows between them. The net result is that electrons move *toward* the surface. This attracts the positive ion cores closer to the rest of the crystal.

The other two explanations of outer-layer contraction are closely related. The second emerges from the effective-medium theory (EMT) of metallic bonding.[3] In EMT, to lowest order, an atom of atomic number Z prefers a location where the electron densities associated with its neighbors sum to an optimal value that depends only on Z. This value is a compromise between the atom's tendency to be located in a region of high density, in order to maximize electron ion-core interactions, and to be located in a region of low density in order to minimize the kinetic energy that results from the orthogonalization requirement of the Pauli exclusion principle. In the EMT picture, when a crystal is truncated to form a surface, the surface atoms find that the electron density provided by their neighbors is reduced, for the simple reason that several neighbors are missing. They move in such a way as to return to the optimal electron density. Since they need to find positions where the electron density is higher, they move toward the rest of the crystal.[4]

The third explanation for outer-layer contraction is that it is a natural consequence of the chemists' concept of bond-order–bond-length correlation.[5] Here the operative principle is saturation of valence. Every atom has a fixed number of valence electrons. As an atom's coordination increases, those electrons must be distributed into a larger number of bonds. The number of valence electrons in each bond is therefore reduced, and the bond length therefore increases. Reversing this argument, if a surface is formed, the surface atoms lose several neighbors. The electrons that were involved in bonding to these neighbors therefore redistribute themselves nearer (i.e., they "back-bond") to the atoms in the layer below. This strengthens the bond between the first and second atomic layers, and reduces their separation.

Most of the surfaces whose structure has been analyzed obligingly obey these simple physical arguments.[6] A few do not, and either expand very slightly or remain "ideal." Typically these surfaces are closed packed. This means that the outer-layer atoms are missing relatively few neighbors, and that their electron densities undergo very little Smoluchowski smoothing. (Their charge densities are very weakly corrugated to begin with.) For these surfaces, therefore, both the increase in back-bond strength due to loss of surface atom coordination, and the electrostatic forces tending to contract the outer-layer separation *should* be relatively small. The sign and magnitude of the relaxation of these closed-packed metal surfaces is therefore a matter of "details" of the surface electronic structure. Such details are, arguably, too complex to try to explain via simple physical ideas.

The work reported here is aimed at rationalizing the behavior of the Be(0001) surface relative to this seemingly complete picture. Recent analysis[7] by low-energy electron diffraction (LEED) implies that the outer-layer separation of this close-packed, simple-metal surface is not just slightly expanded, *but by close to 6% relative to "ideal."* In what follows, I point out this failure of the above "simple arguments" is a consequence of the necessity of promoting an s electron before a closed-shell, group IIA or IIB atom can form a strong bond. "First-principles" electronic structure calculations based on the local-density approximation (LDA),[8] which automatically incorporates the energy of s-electron promotion, are qualitatively consistent with the experimental results, and they show that p- to s-electron demotion accompanies the outward relaxation of the Be(0001) surface.

In the next section of this paper, I discuss the bonding of the group IIA and IIB atoms in relation to simple pictures of metallic bonding. In Sec. III, I present and analyze the results of linearized-augmented-plane-wave (LAPW) calculations[9,10] of the geometric and electronic structure of Be(0001).

II. BONDING OF THE CLOSED-SHELL METALS

From the chemical point of view, the Be atom, whose valence shall contains two 2*s* electrons, is essentially a large, relatively polarizable He. Were it not for the fact that 2*s* to 2*p* promotion in Be costs only 2.72 eV,[11] Be would act as an inert gas. Similar remarks apply to the other group IIA and IIB elements, although *s* to *d* promotion is important in the heavier ones. Whether a Be dimer forms as a molecule more tightly bound than by van der Waals attraction has only recently been determined. The Be-Be bond *is* covalent,[12] but the scission energy is only 0.10 eV while the bond length is 4.658 bohr,[13] 11% *longer* than the nearest-neighbor distance in bulk Be. The reason that Be_2 is so weakly bound is that the energetic compensation for 2*s* to 2*p* promotion, in the form of additional electron ion-core attraction, is not very large. This is because each Be ion core has a positive charge of only 2, and that charge is partially screened by the valence electrons that remain nearby. The consequence is that Be does not obey the usual bond-order–bond-length correlation (see Table I). Increasing the number of neighbors from 1 in the dimer to 12 in bulk Be causes the bond length to become 10% shorter, while the cohesive energy per bond increases by more than a factor of 5. With this in mind, it is not surprising that reducing the number of neighbors to a Be, by forming a surface, causes its bonds to *lengthen*. Similar arguments may be expected to apply to the other group IIA and IIB metals, taking account of variations in *s* to *p* and *s* to *d* promotion energies, atomic sizes, and polarizabilities. Table I shows that *these metals universally violate the usual bond-order–bond-length correlation, while open-shell metals obey it.*

TABLE I. Comparison of homonuclear dimer bond lengths with nearest-neighbor separations in the corresponding elemental crystals. Notice that the group IIA and IIB metals are the only ones for which the dimer bond is longer than the nearest-neighbor spacing in the solid. See Ref. 14 for sources of the dimer information (NN denotes nearest-neighbor).

Atom	Group in Periodic Table	Dimer bond length (a.u.)	Bulk NN distance (a.u.)	Ratio
Li	IA	5.05	5.71	0.884
Na	IA	5.82	6.91	0.842
K	IA	7.38	8.55	0.863
Cs	IA	8.3	9.89	0.84
Be	IIA	4.66	4.20	1.11
Mg	IIA	7.35	6.05	1.22
Ca	IIA	8.08	7.46	1.08
B	IIIA	3.00	3.16 (α boron)	0.952
Al	IIIA	4.66	5.40	0.863
Bi	VA	5.03	5.80	0.867
Cu	IB	4.20	4.84	0.867
Ag	IB	4.78	5.46	0.875
Au	IB	4.67	5.44	0.858
Zn	IIB	7.56	5.03	1.50
Cd	IIB	9.10	5.63	1.62
Hg	IIB	6.86	5.69	1.21
Fe	VIIB	3.82	4.69	0.814
Ru	VIIB	4.57	5.01	0.912

The related semiempirical methods known as effective-medium theory,[3(a)] the quasiatom method,[3(b)] and the embedded-atom method[3(c)] are physically transparent, and computationally simple. Therefore it is important to learn how to extend them to as many materials as possible. From the perspective of the lowest-order EMT, Be is virtually inert. According to the atom in jellium calculations of Puska, Niemenen, and Manninen,[15] the competition between electron binding to the (smeared out) ion cores and Pauli repulsion results in an optimum electron density for Be of less than 0.0005 e/bohr^3. This implies a large nearest-neighbor distance for bulk Be compared to the experimental value of 4.20 bohrs.

The reason for this result is that the calculation of Puska, Niemenen, and Manninen[15] is for an atom immersed in a *homogeneous* electron gas. The positive charge in this case is totally isotropic, which has the consequence that there is insufficient energetic compensation for promotion of valence *s* to *p* electrons. Although it is not obvious how to remedy this problem in the EMT, it *is* easy to see how one might proceed in a more empirical embedded-atom-method (EAM) description of the Be(0001) surface.[16] The idea is to replace the usual empirical function, which describes the energy of the embedded atom versus the local electron density, by an embedding function with an additional independent variable to represent the degree of *s* to *p* excitation. This will provide a variational degree of freedom that represents the competition between the cost of promoting an *s* electron and the binding energy gained by doing so.

Consider embedding a promoted Be, a Be*, in a crystal. Such a species will bond strongly and will therefore have an embedding function whose minimum is deeper and whose optimal electron density is higher than that corresponding to the ground-state atom. On the other hand, the embedding function for the Be* will be rigidly shifted up by the energy that the promotion costs. In this scheme, Be will choose its experimental bulk lattice parameter by maximizing *s* to *p* promotion to take maximum advantage of the possibility of interaction with 12 nearest neighbors. At the (0001) surface, however, since the outer layer Be's are missing three nearest neighbors, the energy optimization will reduce the number of p_σ electrons, because the cost of their promotion is no longer adequately recompensed. This will shift the electron density optimization to an embedding curve that is more like the one for ground-state Be, whose minimum lies at a lower electron density. Thus the outer-layer Be's will move away from the crystal, where the electron density contributions of the second layer are reduced.

Although these ideas may seem reasonable, before attempting to construct an approximate LDA theory of the Be(0001) surface, which is what the EAM purports to be, it would be prudent to verify that a complete solution of the LDA for Be(0001) actually produces the experimental surface layer expansion, at least "semiquantitatively." A state-of-the-art first-principles calculation is the subject of what follows.

III. LAPW CALCULATIONS FOR Be(0001)

Results of LAPW calculations for bulk Be and the Be(0001) surface are presented in this section. The computational scheme and computer code of Hamann[10] were used, wherein the one-electron potential is not subject to any shape approximation. Exchange and correlation effects were represented via the LDA based on the Wigner interpolation formula.[17] Both the first and second interlayer separations at a Be(0001) surface are predicted to expand, by 3.9% and 2.2%, respectively, relative to "ideal." That a substantial outer layer expansion should occur agrees with the LEED analysis of Davis *et al.*[7] However, quantitative agreement with the experimentally preferred values of 5.8%, -0.2%, and 0.2% for the relative changes of the first three interlayer separations is less than perfect. This is presumably because the softness of the Be(0001) surface force constants makes it significant, as discussed in Sec. III B, that the experiment was performed at room temperature, while the LAPW results correspond to $T=0$ K. The most compelling explanation for the outward-surface relaxation emerges from an analysis of the angular momentum decomposition of the electron occupations of the LAPW muffin tins. This is presented in Sec. III D.

A. Bulk-lattice parameters

An earlier study, for Rh(001),[18] showed that the relation between calculated surface relaxation and assumed in-plane lattice parameter is such as to conserve the volume occupied by a surface atom. Thus, if one begins a calculation of surface relaxation by fixing the bulk lattice in its experimental geometry, the relaxation can differ substantially from what it would be if one adopted the more consistent approach, namely, determining the bulk lattice geometry by optimizing the LDA energy of the bulk crystal. I therefore begin the Be(0001) surface relaxation study by minimizing the LDA energy for bulk hcp Be as a function of a and c, the lengths of the fundamental translation vectors. The orbital basis for the bulk Be calculations includes all LAPW's of plane-wave wave-vector square up to 10.0 a.u. The irreducible $\frac{1}{24}$ of the Brillouin zone is sampled with 42 Bloch vectors, i.e., 14 equally spaced Bloch vectors in each of 3 equally spaced planes perpendicular to the c axis. I use plane waves of wave-vector square up to 100 a.u. in solving Poisson's equation, and allow for angular momenta up to $l=6$ in the muffin tins, both for wave functions and the charge density. I use a muffin-tin radius of 1.9412 bohr; this is small enough that the muffin tins do not overlap for over a substantial range of crystal geometries. To find the lowest-energy crystal geometry, I fit the most general cubic polynomial in a and c (comprising 10 terms) to the total energies computed for 13(a,c) pairs, as set forth in Table II. The minimum of the cubic energy surface lies at $a=4.270$ bohrs and $c=6.777$ bohrs, in good agreement with the experimental values, $a=4.29$ bohrs and $c=6.78$ bohrs. I use the former values for the surface calculations.

TABLE II. Valence electron energy (in hartrees per unit cell) of hcp Be vs a and c, the lengths (in a.u.) of the lattice translation vectors.

a (a.u.)	c (a.u.)	E_{valence} (hartree)
4.290	6.784	$-2.305\,797$
4.290	6.634	$-2.305\,495$
4.290	6.934	$-2.305\,460$
4.140	6.784	$-2.304\,409$
4.140	6.634	$-2.304\,144$
4.140	6.934	$-2.304\,136$
4.440	6.784	$-2.303\,917$
4.440	6.634	$-2.303\,715$
4.440	6.934	$-2.303\,529$
4.290	6.484	$-2.304\,435$
4.290	7.084	$-2.304\,532$
3.990	6.784	$-2.299\,189$
4.590	6.784	$-2.300\,371$

B. Surface relaxation

I evaluate the surface relaxation of Be(0001) by minimizing the LDA energy of seven- and nine-layer slabs with respect to the locations of their outer two atomic layers, holding the separations of their central three and five layers, respectively, at the optimal value, 3.389 bohrs, calculated for bulk Be. By performing calculations for two slab thicknesses it is possible to estimate the importance of quantum size effects in the results. The basis set once again includes all LAPW's of plane-wave wave-vector square up to 10.0 a.u. The irreducible $\frac{1}{12}$ of the surface Brillouin zone is now sampled with 14 equally spaced Bloch vectors. I once again use plane waves of wave-vector square up to 100 a.u. in solving Poisson's equation, and allow for angular momenta up to $l=6$ in the muffin tins. Results for the seven- and nine-layer slabs are reported in Tables III and IV, respectively.

If quantum size effects were absent, then the valence electron energy for an n-layer Be(0001) slab would equal nE_B+2E_S, where E_B is the valence energy per atom of bulk Be and E_S is the surface energy. From the results for unrelaxed seven- and nine-layer slabs in Tables III and IV, one finds that $E_B=-1.1532$ hartrees. This is in good agreement with the value obtained from the bulk Be

TABLE III. Valence electron energy (in hartrees per surface unit cell) of a seven-layer Be(0001) slab vs Z_1 and Z_2 (in a.u.), the distances relative to the slab center of the outermost and subsurface atomic planes. Mirror symmetry is maintained with respect to the central plane of the slab.

Z_1 (a.u.)	Z_2 (a.u.)	E_{valence} (hartree)
10.1655	6.7770	−8.033 61
10.3155	6.6270	−8.031 86
10.3155	6.7770	−8.034 50
10.3155	6.8520	−8.034 56
10.3155	6.9270	−8.033 84
10.3905	6.7020	−8.033 11
10.3905	6.8520	−8.034 74
10.4655	6.7770	−8.033 75
10.4655	6.8520	−8.034 54
10.4655	6.9270	−8.034 59
10.4655	7.0020	−8.033 93

calculation, $E_B = -1.1529$ hartrees, providing evidence that quantum size effects are small.

To determine the optimal geometry of the seven-layer film, I perform a least-squares fit of the most general cubic polynomial to the energies calculated for 11 sets of Z_1 and Z_2, the distances of the outer two film layers from the central layer (cf., Table III). The LDA energy is minimized, according to the fit, for $Z_1 = 10.390$ bohrs and $Z_2 = 6.853$ bohrs. This corresponds to a relative expansion of the separation of the outer two layers, $\Delta Z_{12}/3.389$ bohrs$=4.4\%$, and of the second and third layers, $\Delta Z_{23}/3.389$ bohrs$=2.2\%$. A similar least-squares fit is performed for 12 sets of outer-layer positions for the nine-layer film (cf. Table III). In this case the minimum energy is achieved when $Z_1 = 13.7603$ bohrs and $Z_2 = 10.2405$ bohrs. This corresponds to a relative expansion of the separation of the outer two layers, $\Delta Z_{12}/3.389$ bohrs$=3.9\%$, and of the second and third layers, $\Delta Z_{23}/3.389$ bohrs$=2.2\%$. The fact that the calculated relaxations are very similar for the seven- and nine-layer slabs again indicates that quantum size effects are small.

TABLE IV. Valence electron energy (in hartrees per surface unit cell) of a nine-layer Be(0001) slab vs Z_1 and Z_2 (in a.u.), the distances relative to the slab center of the outermost and subsurface atomic planes. Mirror symmetry is maintained with respect to the central plane of the slab. The values $Z_1 = 13.7603$ a.u. and $Z_2 = 10.2405$ a.u. optimize the energy. Charge-density and electron energy-level dispersions shown below correspond to this geometry.

Z_1 (a.u.)	Z_2 (a.u.)	E_{valence} (hartree)
13.5540	10.1655	−10.340 03
13.5540	10.2405	−10.339 16
13.6290	10.1280	−10.340 38
13.6290	10.2030	−10.340 49
13.7040	10.1655	−10.340 68
13.7040	10.2030	−10.340 82
13.7040	10.2405	−10.340 54
13.7603	10.2405	−10.340 85
13.7790	10.1280	−10.339 92
13.7790	10.2030	−10.340 71
13.8540	10.1655	−10.339 76
13.8540	10.2405	−10.340 54

The LEED analysis of Davis *et al.*[7] implies a 5.8% expansion of the outer-layer separation of Be(0001) and is consistent with no relaxation of the separation of the second and third atomic layers. These results are evidently not in perfect agreement with the conclusions drawn from the LAPW energies. Nevertheless, the fact that the LAPW implies a substantial, roughly 4%, expansion of the outer-layer separation shows that the calculation does embody the main qualitative feature of the experimental result, and should provide a foundation for understanding the physics of the "anomalous expansion" of the Be(0001) surface.

The quantitative discrepancy between the LEED analysis of Be(0001) and the LAPW results does, incidentally, appear to have an obvious source. Although the fits of LEED theory to experimental I-V profiles of Davis *et al.* are very good, "in the same league with those of better LEED analyses," the data that were analyzed were taken at room temperature, while the LAPW results apply to $T=0$ K. As is noted in Sec. III C, immediately below, both the LAPW evaluation of the surface energy, and the LEED data indicate that the surface phonons of Be(0001) are very soft. This has two consequences: (1) inadequate knowledge of how to incorporate surface phonon corrections into the room-temperature LEED analysis may have given rise to systematic errors at a level that is considerably worse than might be anticipated for crystals whose surface force constants are larger; and (2) even if the 300-K LEED analysis were perfect, the outermost interlayer separations at that temperature *should have been significantly different from their values at $T=0$ K.* The easiest way to provide a more stringent test of the accuracy of the LDA results would likely be to redo the LEED experiment and analysis at a low temperature.

C. Surface energy

Using 1.1532 hartrees for the valence energy per atom of bulk Be, the surface energy of the relaxed nine-layer Be(0001) film is calculated to equal 0.0190 hartrees, or 0.52 eV per surface atom, while that of the unrelaxed film is 0.0194 hartrees, or 0.53 eV per atom. Thus the anomalously large expansion of the Be outer-layer separation involves a gain of a rather small energy, roughly 0.012 eV per surface atom. This agrees with the finding in the LEED analysis of a low surface Debye temperature, implying soft surface phonons. A value of 0.31 eV/atom is quoted by Murr[19] for the surface energy of Be at its melting point. The level of disagreement between this value and that calculated via the LAPW is characteristic of LDA surface energy calculations, perhaps slightly worse.[20]

D. Electronic charge density vs outer-layer expansion

One might expect an analysis of the electron density of a Be(0001) slab to help explain the large expansion at the surface. Figure 1 compares the densities of the ideal and relaxed slabs in the $(11\bar{2}0)$ plane, which is normal to the surface, passing through a first-layer nucleus and a nearest-neighbor nucleus in the second layer. The main difference that one sees in comparing the two plots is that as a result of the expansion of the outer atomic layers, the electron density drops in the surface region. This shows that the expansion is not a consequence of increased "back-bonding" of the outer Be layers to the layers below, but otherwise does not provide much insight.

More can be learned from Table V, where I compare the angular momentum decomposition of the number of electrons in the LAPW muffin tins, of the ideal and relaxed nine-layer slabs. Since s-p hybridization is essential to the cohesion of Be, one expects that the ratio of p- to s-electron charge in the outer-layer muffin tins will decrease as they relax away from the rest of the slab. This *is* what happens, but not in the way one might at first imagine. Table V shows that when relaxation occurs, the s and p_π occupations of the outer-layer muffin tins undergo changes of less than 1%. *At the same time the p_σ population decreases by almost 8%.* (Here p_σ and p_π are defined relative to the surface normal.) This behavior is the consequence of two phenomena that simultaneously accompany expansion of the outer-layer spacing. The first is decreasing overlap of second-layer orbitals with first-layer muffin tins, which results in a decrease of both the s and p_σ muffin-tin charges, but by symmetry, no change in

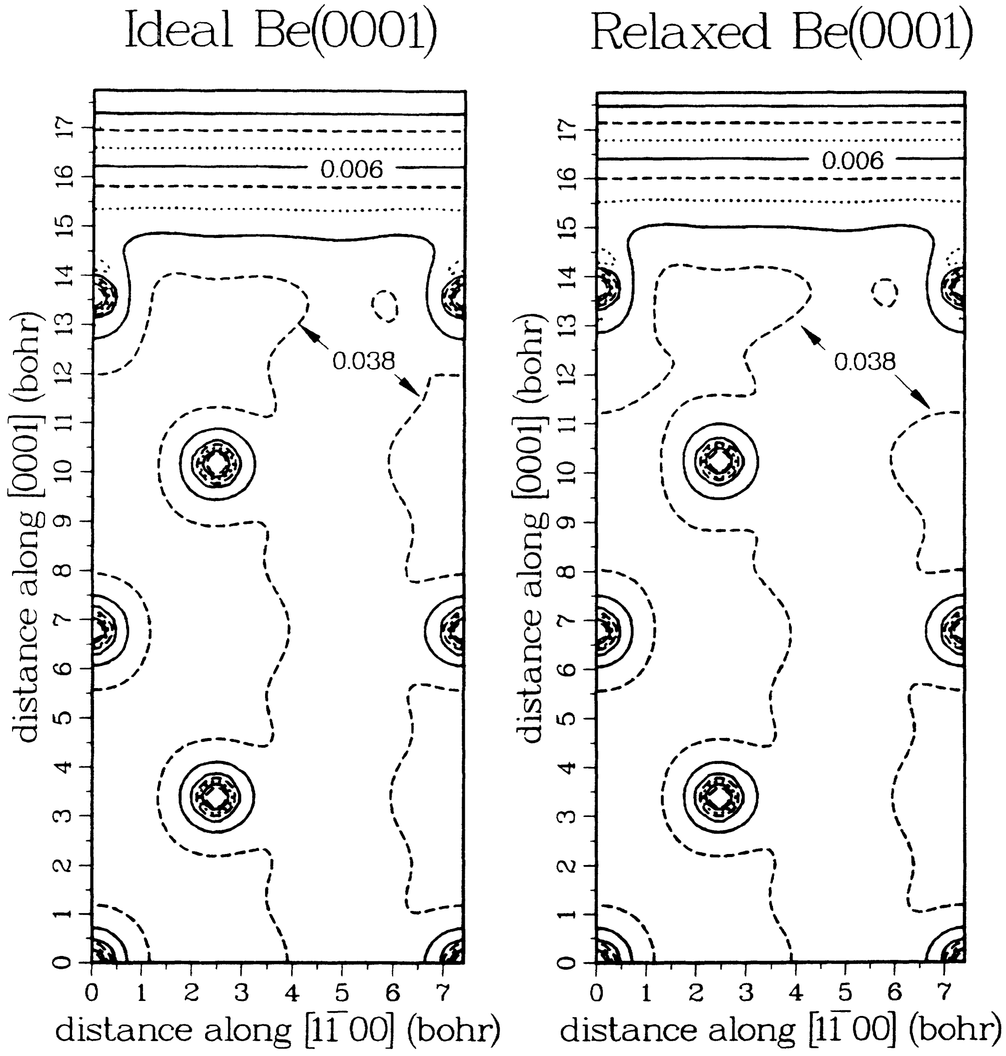

FIG. 1. Charge-density contours in the $(11\bar{2}0)$ plane, for nine-layer ideal and relaxed Be(0001) slabs. The vacuum lies at the top of the plot. Labels are in e/bohr^3. Successive contours correspond to changes of a factor of $10^{1/5}$. Notice the relative shrinkage of the contour labeled 0.038, in the outer two interlayer spaces of the relaxed slab. It shows that relaxation is accompanied by a reduction of the interlayer electron density in the surface region.

TABLE V. Integrated electron number densities in the muffin tins of the "ideal" and the relaxed nine-layer Be(0001) slabs, decomposed according to angular momentum symmetry. Also the percentage decrease in these angular momentum resolved electron numbers as a result of relaxation. The "ideal" slab corresponds to $(Z_1,Z_2)=(13.5540,10.1655)$ a.u., while the relaxed slab has $(Z_1,Z_2)=(13.7603,10.2405)$ a.u.

	Surface layer	Subsurface layer	Layer 3	Layer 4	Central layer
$\rho_{\text{ideal}}(s)$	0.3714	0.3812	0.3729	0.3698	0.3697
$\rho_{\text{relaxed}}(s)$	0.3699	0.3747	0.3700	0.3699	0.3693
% decrease	0.40%	1.7%	0.78%	−0.03%	0.11%
$\rho_{\text{ideal}}(p_\sigma)$	0.1631	0.2453	0.2501	0.2495	0.2497
$\rho_{\text{relaxed}}(p_\sigma)$	0.1504	0.2297	0.2441	0.2492	0.2489
% decrease	7.8%	6.4%	2.4%	0.12%	0.32%
$\rho_{\text{ideal}}(p_\pi)$	0.4610	0.4770	0.4823	0.4899	0.4858
$\rho_{\text{relaxed}}(p_\pi)$	0.4580	0.4704	0.4804	0.4860	0.4869
% decrease	0.65%	1.4%	0.39%	0.80%	−0.23%

the p_π. The second is demotion of p_σ to s electrons. This obviously means an increase in the s occupation of the outer muffin tins, a decrease in the p_σ population, and a slight change in the p_π's owing to changes in screening of the cores. Summing these effects, one understands why outward relaxation is accompanied by small changes in the s and p_π occupations of the outer-layer muffin tins and a decrease in their p_σ population that is substantial by comparison.

Relaxation also affects the muffin-tin population of the subsurface layer substantially, and again the effect is a sum of contributions from overlap reduction and of the demotion of p_σ to s electrons. Since subsurface layer atoms remain coordinated to six Be's in layers 1 and 3, one might expect that their muffin tins would suffer a somewhat smaller reduction of p_σ population, as a result of relaxation, than the surface layers do. At the same time, since the subsurface muffin tins lose overlap of wave-function tails from both outer- *and* third-layer Be's, the net reduction of s occupation should be enhanced, which is what Table V shows.

One should note that although surface-layer demotion of p_σ to s electrons is linked to relaxation, the same effect is already evident in the results for the ideal surface. Thus notice that while the s and p_π occupations of the outer-layer muffin tin of the ideal slab are within a few percent of the corresponding occupations in interior layers, its p_σ population is reduced by 35%. Once again this contrast can be interpreted as the sum of effects. Spillout of charge into the vacuum as well as the absence of overlapping wave-function tails from a layer above both imply a reduction of the s and p_σ populations of the outer-layer muffin tin. However, at the same time p_σ to s demotion is energetically favorable, because of the reduced coordination of surface layer atoms. Adding these effects, one can understand why the net s occupation of the outer-layer muffin tin is only slightly different from that in the interior, while the p_σ population decreases sharply.

E. Surface electronic level dispersion

Electron energy levels for the Be(0001) surface have been measured by Bartynski *et al.*[21] using angle-resolved ultraviolet photoemission spectroscopy (UPS). Level dispersions and the corresponding wave functions, for an ideal ten-layer Be(0001) slab, have been calculated, and are described in detail by Chulkov, Silkin, and

TABLE VI. Energies E_1 and E_2 (in eV relative to the Fermi energy) of occupied surface states vs wave vector, for the relaxed Be(0001) film. These values correspond to the solid dots below the Fermi level in Fig. 3. There are two surface states at each wave vector because the slab has two surfaces. The splitting of the two surface-state energies reflects the overlap of the tails of the surface-state wave functions in the interior of the slab.

k	E_1 (eV)	E_2 (eV)
$\bar{\Gamma}$	−2.83	−2.72
$\frac{1}{9}\bar{M}$	−2.73	−2.61
$\frac{2}{9}\bar{M}$	−2.43	−2.30
$\frac{3}{9}\bar{M}$	−1.96	−1.78
$\frac{4}{9}\bar{M}$	−1.32	−1.07
$\frac{5}{9}\bar{M}$	−0.61	−0.18
$\frac{8}{9}\bar{M}$	−1.56	−1.56
$\bar{M}$	−1.85	−1.85
$0.8\bar{M}+0.2\bar{K}$	−1.74	−1.74
$0.6\bar{M}+0.4\bar{K}$	−1.41	−1.41
$0.4\bar{M}+0.6\bar{K}$	−0.88	−0.88
$0.2\bar{M}+0.8\bar{K}$	−0.24	−0.24
$\bar{K}$	−0.47	−0.47
$\frac{6}{12}\bar{K}$	−0.40	+0.04
$\frac{5}{12}\bar{K}$	−1.07	−0.78
$\frac{4}{12}\bar{K}$	−1.67	−1.47
$\frac{3}{12}\bar{K}$	−2.17	−2.01
$\frac{2}{12}\bar{K}$	−2.53	−2.40
$\frac{1}{12}\bar{K}$	−2.75	−2.64

Shirykalov.[22] In Figs. 2 and 3, again in the hope of extracting information regarding the forces that lead to the anomalous surface interplanar expansion, I compare the electron energy-level dispersions that emerge from the LAPW calculations for the ideal and the relaxed nine-layer Be(0001) slabs. States whose wave functions are strongly surface localized are indicated as solid circles. (Numerical values of the energies of these states, for the relaxed slabs, are given in Table VI.) The other states are represented by open circles.

Agreement between the measured and calculated surface state energies (cf. Fig. 3) is excellent, apart from the measured surface state that lies virtually at the bulk band edge at $\bar{M}$ (~ 3 eV below the Fermi level) and disperses up as one moves toward $\bar{\Gamma}$. Chulkov's calculations predict a band of "unusual" surface states, dispersing up from -2.9 eV at $\bar{M}$, that track the upper edge of the lowest band of bulk states to $\bar{K}$. These surface states are unusual in that their weight is concentrated in the third atomic layer at $\bar{M}$, starting inward from the surface, and shifting gradually to the second layer as one moves toward $\bar{K}$. A similar band is predicted by the present calculations, for both the ideal and relaxed Be(0001) slabs. Assuming that this band corresponds to the lower surface state near $\bar{M}$ of Bartynski *et al.*, it is puzzling that it should appear in the UPS at $\bar{M}$, where its weight is mainly three layers down, and not at $\bar{K}$, where its weight is concentrated in the second atomic layer. In a more recent UPS study,[23] satisfyingly, this unusual, deep surface band is not only present at $\bar{K}$, but most of the way from $\bar{K}$ to $\bar{M}$.

Of the two bands of surface states lying in the wide gap between the bulk s and p bands, the one that starts from $\bar{\Gamma}$ near -3 eV and disperses up as one moves toward $\bar{M}$ or $\bar{K}$ is essentially an s-p_σ band. The state which disperses up from near -2 eV at $\bar{M}$ is a p_π state, strongly localized on surface layer atoms. The fact that the band starting from $\bar{\Gamma}$ appears to be a doublet is the result of interaction of surface states associated with the two different sides of the slab. The fact that this splitting is invisible in the case of the band that disperses up from $\bar{M}$ corresponds to the fact that this band is considerably more localized in the surface region.

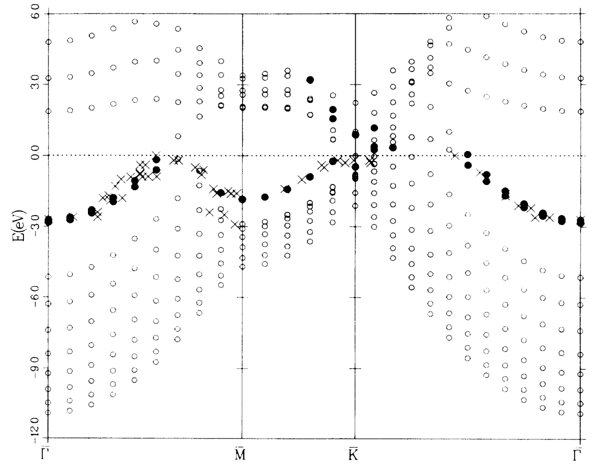

FIG. 3. Electron energy-level dispersion curves for the relaxed nine-layer Be(0001) slab. Experimental points, from Ref. 21, are represented as ×'s.

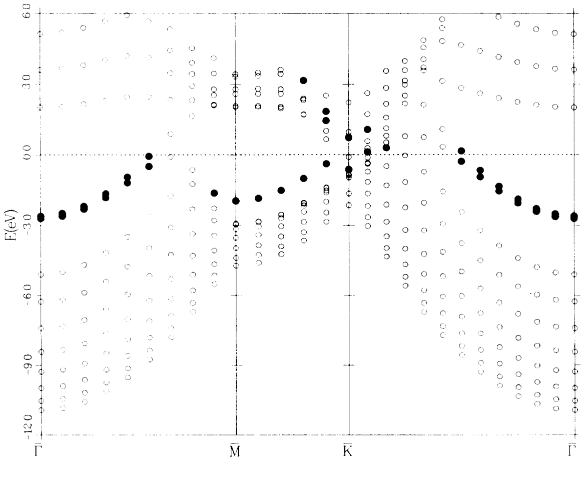

FIG. 2. Electron energy-level dispersion curves for an ideal nine-layer Be(0001) slab.

Comparing Figs. 2(a) and 2(b), one observes that relaxation causes the s-p_σ surface band to shift slightly downward, while the p_π band shifts upward. In both cases, the shifts are small, of the order of 0.1 eV, but an order of magnitude larger than the total energy shift per atom associated with the relaxation. It is hard to draw any clear conclusion from these shifts in the band that might "explain" the anomalous expansion of the surface.

The work function calculated for the relaxed, nine-layer film is 5.54 eV. This is in moderate agreement with the measured lower bound of 5.10 eV.[24] The level of accuracy of measured work functions is, of course, never very clear. This fact, together with the systematic errors in the LDA that are responsible for the quantitative differences between measured and predicted outer layer geometries, can certainly account for the 0.4-eV discrepancy.

IV. DISCUSSION

In the foregoing, the anomalously large expansion of the outermost layer spacing of Be(0001) is attributed to the facts that Be is a closed-shell atom, and that it is energetically less profitable to promote s to p_σ electrons on surface layer Be's than on interior Be's because of the loss of three nearest neighbors. This scenario should also apply to the other closed-shell metals, though their promotion energies and the proximity of d levels may result in quantitative differences. It is of considerable interest to see whether this generalization is valid, and whether, for example, a correlation can be established between the ratios of dimer bond length to nearest-neighbor distance for the various metals (cf., Table I) and the magnitudes of their surface layer expansions. The result of this work, one would hope, will be a *really* complete understanding of the physics of metal surface layer relaxation.

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